Electrochemical Co-Depositing of Pt, Pt/Mo, Pt/Ru and Pt/Ru/Mo Electrodes and Their Characterization by Surfaces Sciences

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Interest in nanoscopic platinum particles derives mostly from the importance of highly dispersed platinum in catalysis. Many gas-phase catalytic processes exhibit a pronounced particle size dependence of the catalytic activity, and evidence for a particle size effect in electrochemical reactions, such as the methanol oxidation and oxygen reduction reactions. Carbon-supported platinum particles are widely used as electrocatalysts,[1,2] e.g. for fuel oxidation and oxygen reduction in low temperature fuel cells. Considerable efforts were made in order to correlate the catalytic activity of such electrodes with their morphology. Usually by characterizing the catalyst particles within rather complex composite electrodes.[3]

Several methods have been taken for the preparation of platinum particles such as colloid-coating, vacuum evaporated deposition and electrodeposition. We used the, electrodeposition method, due to its feasibility to control the size and loading of particles, and use highly oriented pyrolytic graphite (HOPG) like substrate to prepare Pt/HOPG, Pt/Mo/HOPG, Pt/Ru/Mo/HOPG electrodes. The electrochemical experiments were carried out at room temperature in a three-electrode electrochemical cell constructed of Teflon with a Viton O-ring. The working electrode was a Highly Oriented Pyrolytic Graphite (HOPG) surface from Advanced Ceramics (12mmx12mmx12mm) which had a fresh surface prior to each experiment by cleaving with adhesive tape. The counter electrode was a platinum gauze. A $Hg|Hg_2SO_4$, K_2SO_4 (saturated) electrode was used as the reference (0.64 V vs. NHE or 0.40V vs. SCE), all solutions were prepared with a Nanopure system (Barnstead) giving water with a resistivity of $18M\Omega^{-cm}$. Before each electrodeposition experiment, several voltammograms (-0.8 to 1.0 V at 20mV s^{-1},5cicles) were recorded in 0.5M H_2SO_4 to ensure that HOPG surface is free of metals and to control the reproducibility of the surface area of the electrode. The electrodeposition of solutions was done with,$Pt(1mMK_2PtCl_6/0.5MH_2SO_4)$,$Pt/Mo(1mMK_2PtCl_6/0.05MNa_2MoO_4.2H_2O/0.5MH_2SO_4)$,$Pt/Ru(1mMK_2PtCl_6/0.05MRu(C_5H_7O_2)_3/0.5MH_2SO_4)andPt/Ru/Mo(1mMK_2PtCl_6/0.05MRu(C_5H_7O_2)_3/0.05MNa_2MoO_4.2H_2O/0.5MH_2SO_4)$, on HOPG. After electrodeposition, the electrodes were removed from the cell, gently rinsed O_2-free Milli--Q water, and finally dried under N_2 at room temperature.

The topography of the working electrodes were studied at the nanometer atomic resolution ranges by Scanning Tunneling Microscopy (STM), and AFM, Scanning electron microscope (SEM) measurements were carried out in a JSM 5800 LV system (JEOL), to study the the surface at micrometer resolution. XPS was used to determine the oxidation state of the metals on the surface of the electrodes. After the electrodeposition of the metals on HOPG, and its characterization, electrochemical methanol oxidation studies were done in a solution of 1M CH_3OH/0.5M H_2SO_4 in a potential of –0.453V to 0.497V vs. Hg/Hg_2SO_4, to determine the catalytic activity of these electrodes.

Figure 1 shows the electrodeposition at HOPG the particles nucleate and grow following the well-ordered structure of HOPG taking a geometrical shape of triangles like shows figure 2. In this work we want to get a relationship of the topography of the surface and the catalytic activity of these electrodes for methanol oxidation.

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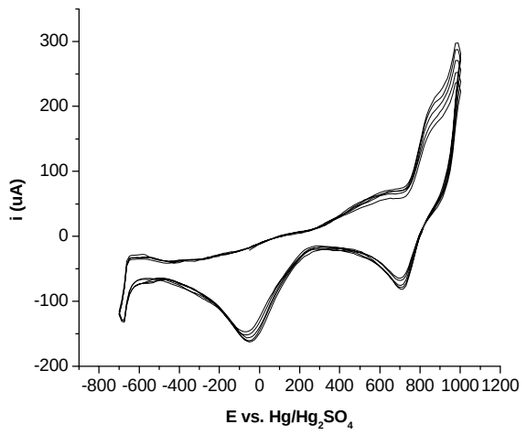

Figure 1 Cyclic Voltammogram of $0.1mMK_2PtCl_6/0.5MH_2SO_4$ on HOPG.

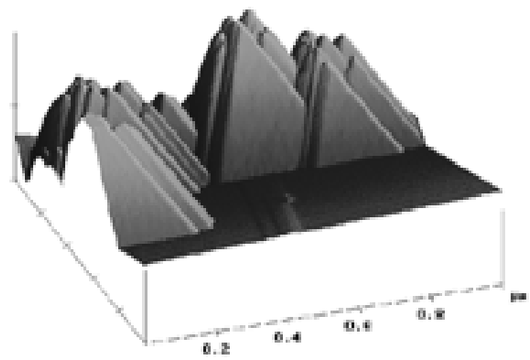

Figure 2 AFM image of Pt/HOPG electrode 10µmx10µm area.

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